



1) Japanese Unexamined Patent Application Publication No.
10-204173

(43) Publication Date: August 4, 1998

(21) Application No. 9-13710

(22) Application Date: January 28, 1997

(71) Applicant: Asahi Kasei Corporation

(72) Inventor: EGUCHI et al.

(54) [Title of the Invention] METHOD FOR REFORMING
POLYPHENYLENE ETHER

(57) [Abstract]

[Object] A method for reforming a polyphenylene ether is provided, wherein the mechanical properties of the polyphenylene ether are improved and, simultaneously, the fluidity is also improved significantly.

[Solving Means] A method for reforming a polyphenylene ether, the method characterized by including the steps of subjecting a phenolic monomer to oxidative polymerization in the presence of a copper compound and at least one type of amine, which serve as catalysts, and in the coexistence of a secondary amine represented by Formula (1) while oxygen is supplied; and heat-treating a slurry, in which a part of the resulting polyphenylene ether is deposited during the polymerization or after the polymerization, at a temperature

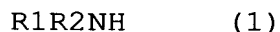
within the range of 50°C to 120°C, at which the polyphenylene ether is not completely dissolved, while the supply of oxygen is stopped.

R₁R₂NH (1)

(Where R₁ represents an alkyl group having the carbon number of 1 to 20 or a substituted alkyl group, and R₂ represents an aryl group or a substituted aryl group.)

[Claims]

[Claim 1] A method for reforming a polyphenylene ether, the method characterized by comprising the steps of subjecting a phenolic compound to oxidative polymerization in the presence of a copper compound and at least one type of amine, which serve as catalysts, and in the coexistence of a secondary amine represented by Formula (1) while oxygen is supplied; and heat-treating a slurry, in which a part of the resulting polyphenylene ether is deposited during the polymerization or after the polymerization, at a temperature within the range of 50°C to 120°C, at which the polyphenylene ether is not completely dissolved, while the supply of oxygen is stopped.



(Where R₁ represents an alkyl group having the carbon number of 1 to 20 or a substituted alkyl group, and R₂ represents an aryl group or a substituted aryl group.)

[Claim 2] The method for reforming a polyphenylene ether according to Claim 1, the method characterized in that the oxidative polymerization is conducted by a slurry polymerization method, and a slurry of the resulting polyphenylene ether is used.

[Claim 3] The method for reforming a polyphenylene ether according to Claim 1, the method characterized in that the oxidative polymerization is conducted by a solution

polymerization method, and a slurry, in which at least a part of the polyphenylene ether is deposited by adding a poor solvent of the polyphenylene ether to the resulting polymerization liquid, is used.

[Claim 4] The method for reforming a polyphenylene ether according to Claim 1, wherein the amount of the coexistent secondary amine represented by Formula (1) is 0.01 to 5 percent by weight relative to the weight of the resulting polyphenylene ether.

[Claim 5] The method for reforming a polyphenylene ether according to Claim 1, wherein the phenolic compound is 2,6-dimethylphenol.

[Claim 6] The method for reforming a polyphenylene ether according to Claim 1, the method characterized in that N-ethylaniline or N-phenylethanolamine is used alone or the two are used in combination as the secondary amine represented by Formula (1).

[Claim 7] The method for reforming a polyphenylene ether according to Claim 1, the method characterized in that the oxidative polymerization is conducted by a continuous polymerization method, and a slurry of the resulting polyphenylene ether is further heat-treated continuously.

[Claim 8] A resin composition comprising the polyphenylene ether produced by the method according to Claim 1.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a new method for reforming a polyphenylene ether. In particular, the present invention relates to a new method for reforming a polyphenylene ether in which a slurry of polyphenylene ether produced by an oxidative polymerization method in the coexistence of a specific secondary amine indicated by the present invention is subjected to a heat treatment at a temperature within the range of 50°C to 120°C, at which the polyphenylene ether is not completely dissolved. According to this reforming method, since it is not necessary to increase a catalyst concentration, the productivity improvement is facilitated. In addition, the thus produced polyphenylene ether is a polyphenylene ether in which excellent mechanical properties and the like of the polyphenylene ether itself have been improved and, simultaneously, the fluidity has also been significantly improved. Therefore, an excellent thermoplastic resin is provided by the combination with a styrene based resin and the like.

[0002]

[Description of the Related Art] A polyphenylene ether produced by oxidative polymerization of a phenolic compound has excellent mechanical properties, electric properties, heat resistance, and the like and, furthermore, has a low

water absorption property. Therefore, in recent years, the polyphenylene ether has been received attention as a thermoplastic engineering plastic. In general, for the polyphenylene ether, methods in which phenolic compounds are subjected to oxidative polymerization through the use of catalysts made by combining metal salts and various amines (Japanese Examined Patent Application Publication No. 42-3195, Japanese Examined Patent Application Publication No. 45-23555, Japanese Unexamined Patent Application Publication No. 64-33131, and the like) have been well known.

[0003] Examples of polymerization methods include various polymerization methods, e.g., batch polymerization, continuous polymerization, solution polymerization, and precipitation polymerization, which have been well known to the industry. In particular, as described in Japanese Unexamined Patent Application Publication No. 63-135423, the activity of the catalyst for a continuous method of the precipitation polymerization is very high as compared with that for the corresponding solution polymerization and the batch polymerization and, therefore, a polymer having a narrow molecular weight distribution can easily be produced under control.

[0004] Polyphenylene ether resins have exhibited previously excellent heat resistance, electrical characteristics, acid resistance, alkali resistance, and the like, and in addition,

have excellent characteristics, e.g., low specific gravities and low water absorption properties. On the other hand, these resins are hard to be melt-molded since the fluidity is low. In order to cover this drawback, the polyphenylene ether resins have been used as alloys with styrene based resins by taking advantage of compatibility between the polyphenylene ether and the polystyrene from long ago.

[0005] However, in this well known method, excellent heat resistance of the polyphenylene ether is traded off. Furthermore, the polyphenylene ether has a drawback of low impact strength as well. In order to improve these drawbacks, many technologies have been proposed, in which impact-resistant polystyrenes containing polybutadiene components have been blended (for example, US Patent No. 3383435).

[0006] In order to keep excellent mechanical properties of the polyphenylene ether, polyphenylene ethers having large molecular weights must remain to some extent in the product polymer after polymerization. Polyphenylene ethers having low molecular weights are required to improve the fluidity. This is self-evident, as described in the example of Japanese Examined Patent Application Publication No. 45-25992. In the above-described patent, a resin composition containing a mixture of polyphenylene ethers exhibiting two types of specific solution viscosity has been proposed.

However, the molecular weight distribution cannot be regulated by the solution viscosity, and undesirably, a very complicated equipment configuration is required in the production when polyphenylene ethers having specific solution viscosities are produced separately and these are mixed. The same holds true for the content disclosed in PCT Japanese Translation Patent Publication No. 4-500094.

[0007] Japanese Unexamined Patent Application Publication No. 48-51098 discloses a method for manufacturing a polyphenylene ether having a wide molecular weight distribution by heating a polymerization reaction liquid at 40°C or more for 30 minutes or more. In the example thereof, a method, in which the position of the main peak of a high molecular weight portion is not changed and a low molecular weight portion is increased, is exemplified. However, this method is conducted in an air atmosphere, and there remains great uncertainty about the safety in a practical, industrial scale. Therefore, undesirably, the step to be conducted becomes complicated and extensive. In the example of the above-described patent, there is another example conducted in a nitrogen atmosphere as an inert gas. In this exemplified method, the position of the main peak of a high molecular weight portion is shifted to a low molecular weight side. Consequently, although the fluidity is improved, the mechanical properties are deteriorated and,

thereby, the control of the reaction condition is very difficult. Furthermore, substantially the same method conducted in a nitrogen atmosphere is also described in Japanese Unexamined Patent Application Publication No. 54-33595. This cannot be said a preferable embodiment for the similar reason. Therefore, in the production, a method for easily improving only the fluidity, while the mechanical characteristics of the polyphenylene ether are maintained, has been required.

[0008]

[Problems to be Solved by the Invention] For the purpose of improving only the fluidity while excellent mechanical characteristics of the polyphenylene ether are maintained, the center position of the main peak of the molecular weight distribution of the polyphenylene ether produced in the polymerization and having a distribution in high molecular weights suitable for maintaining the desired mechanical characteristics must be maintained, and only the low molecular weight portion must be increased. Furthermore, this method must be conducted easily and safely.

[0009] For a method for manufacturing a polyphenylene ether not having the above-described problems, it is described in Japanese Unexamined Patent Application Publication No. 7-278293 that a polyphenylene ether exhibiting excellent fluidity and chemical resistance can be produced by a method

in which the center position of the main peak of the molecular weight distribution of the polyphenylene ether produced in the polymerization and having a distribution in high molecular weights suitable for maintaining the desired mechanical characteristics is maintained, and only the low molecular weight portion is increased. However, it was made clear that deterioration in the impact resistance occurred by this method and, thereby, a problem occurred. That is, whatever the case may be, the molecular weight is inevitably reduced when the polymerization liquid of the polyphenylene ether is heat-treated according to the known technologies. Therefore, the concentration of the active catalyst system required in the polymerization must be increased to maintain the mechanical characteristics. Consequently, the development of a method, in which the molecular weight is not reduced even when the polymerization liquid of the polyphenylene ether is heat-treated and, furthermore, the mechanical characteristics and the fluidity are improved simultaneously, has been desired intensely.

[0010]

[Means for Solving the Problems] The inventors of the present invention conducted intensive research on a method for manufacturing a polyphenylene ether not having the above-described problems and, as a result, the present invention has been completed. That is, the present

invention relates to a method for reforming a polyphenylene ether, the method characterized by comprising the steps of subjecting a phenolic compound to oxidative polymerization in the presence of a copper compound and at least one type of amine, which serve as catalysts, in the coexistence of a secondary amine represented by Formula (1) while oxygen is supplied; and heat-treating a slurry, in which a part of the resulting polyphenylene ether is deposited during the polymerization or after the polymerization, at a temperature within the range of 50°C to 120°C, at which the polyphenylene ether is not completely dissolved, while no oxygen is supplied, as well as a resin composition containing the polyphenylene ether produced by the above-described method.

[0011] According to this method, by heat-treating the polymerization liquid, the center position of the main peak of the molecular weight distribution of the polyphenylene ether produced in the polymerization can be shifted to the high molecular weight side and, simultaneously, the low molecular weight portion can be increased. Therefore, excellent mechanical characteristics of the polyphenylene ether can be improved and, simultaneously, the fluidity can be improved. Furthermore, according to this method, the total molecular weight is hardly changed before and after the heating since the increase in molecular weight and the reduction in molecular weight are coincident. Consequently,

the amount of catalyst to be used is reduced and the productivity improvement is facilitated as well, since there is no need to increase the concentration of the active catalyst system in the reaction system.

[0012] The present invention will be described below in detail. In the present invention, cuprous salts, cupric salts, and mixtures thereof can be used as the copper compound. Although any cuprous or cupric compound can be used, a soluble copper salt is preferable from the viewpoint of economy and availability of the compound. Alternatively, even compounds of insoluble (cuprous, cupric) salts can usually be used.

[0013] Examples of cupric compounds usable as the catalyst component of the present invention can include cupric chloride, cupric bromide, cupric sulfate, cupric nitrate, cupric acetate, cupric azide, and cupric toluylate, although not limited to these examples. Examples of usable cuprous compounds can include cuprous chloride, cuprous bromide, cuprous sulfate, cuprous nitrate, cuprous acetate, cuprous azide, and cuprous toluylate, although not limited to these examples. Among them, preferable cuprous and cupric compounds are cuprous chloride, cupric chloride, cuprous bromide, and cupric bromide. These copper compounds may be synthesized from a halogen or an acid corresponding to the oxide, the carbonate, the hydroxide, or the like when the

copper compounds are used.

[0014] The usage of the copper compound is not specifically limited. However, the copper compound can be used appropriately within the range of 0.002 to 0.5 mol in terms of copper relative to 100 mol of phenolic compound, and preferably of 0.005 to 0.2 mol. Examples of at least one type of amine to be used in the present invention can include two amines, that is, at least one type of tertiary alkylendiamine and, if necessary, at least one type of aliphatic secondary amine, and a combination of at least one type of secondary alkylendiamine, at least one type of tertiary amine and, if necessary, at least one type of aliphatic secondary amine. However, the present invention is not limited to these examples.

[0015] Examples of tertiary alkylendiamine can include N,N,N',N'-tetramethylethylenediamine, N,N,N',N'-tetramethylpropane-1,3-diamine, and N,N,N',N'-tetramethylbutane-1,4-diamine. The amount of the tertiary alkylendiamine is not specifically limited. However, 0.1 to 10 mol relative to 100 mol of phenolic compound is used, and 1 to 6 mol is preferable.

[0016] Examples of secondary alkylendiamine can include N,N'-di-t-butylethylenediamine, N,N'-di-t-acylethylenediamine, and N,N'-di-t-isopropylethylenediamine. The amount of the secondary alkylendiamine is not

specifically limited. However, 0.5 to 10 mol per copper atom is used, and 1 to 4 mol is preferable.

[0017] Examples of tertiary amines can include trimethylamine, tripropylamine, tributylamine, diethylmethylaniline, and dimethyl-n-butylamine. Furthermore, tertiary polyamines, e.g., N,N,N',N'-tetraalkylalkylenediamine, can also be used. The amount of the tertiary amine is not specifically limited. However, 0.1 to 10 mol relative to 100 mol of phenolic compound is used, and 1 to 6 mol is preferable.

[0018] Examples of aliphatic secondary amines can include alkyl secondary amines, e.g., dimethylamine, diethylamine, diisopropylamine, and di-n-butylamine; cyclic hydrocarbon secondary amines, e.g., dicyclohexylamine; alicyclic secondary amines, e.g., piperidine, piperazine, and morpholine; secondary alkanolamines, e.g., diethanolamine and diisopropanolamine; and N-alkylalkanolamines, e.g., N-methylethanolamine, N-ethylethanolamine, and N-t-butylethanolamine. The amount of the aliphatic secondary amine is not specifically limited. However, 0.01 to 1 mol relative to 100 mol of phenolic compound is used, and 0.01 to 0.1 mol is preferable. The coexistence of such an aliphatic secondary amine is not always advantageous since the center position of the main peak of the molecular weight distribution of the present invention is further shifted to

the high molecular weight side. Therefore, the usage must be controlled at a minimum amount.

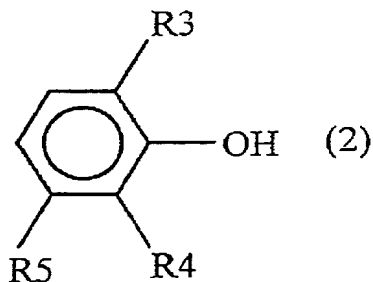
[0019] Furthermore, a halide, a halogen, a hydrogen halide, or a mixture thereof can be used like a promoter, although not limited to them. In the present invention, R1 bonded to nitrogen of the secondary amine represented by Formula (1) represents an alkyl group having the carbon number of 1 to 20 or a substituted alkyl group. The alkyl group is a group, e.g., a methyl group, an ethyl group, a n-propyl group, and an iso-propyl group, in which an aliphatic hydrocarbon is to be bonded. The substituted alkyl group is a group, e.g., a hydroxymethyl group, a 2-hydroxyethyl group, a benzyl group, and a 2-phenylethyl group, in which a part of an aliphatic hydrocarbon has been substituted with a hydroxyl group, an aryl group, or the like. On the other hand, R2 represents an aryl group or a substituted aryl group. The aryl group is a group, e.g., a phenyl group and a naphthyl group, in which an aromatic hydrocarbon is to be bonded. The substituted aryl group is a group, e.g., an (o-, m-, p-chloro)phenyl group and an (o-, m-, p-methyl)phenyl group, in which a part of an aromatic ring has been substituted with a halogen, an alkyl group, or the like. Examples of secondary amines used here can include N-allylalkanolamines, e.g., N-phenylethanolamine, N-(o-methyl)phenylethanolamine, N-(m-methyl)phenylethanolamine, N-(p-

methyl)phenylethanolamine, N-(2',6'-dimethyl)phenylethanolamine, N-(p-chloro)phenylethanolamine, N-(m-chloro)phenylethanolamine, N-(o-chloro)phenylethanolamine, N-(p-ethyl)phenylethanolamine, N-(m-ethyl)phenylethanolamine, and N-(o-ethyl)phenylethanolamine; and N-hydrocarbon-substituted anilines, e.g., N-methylaniline, N-ethylaniline, N-propylaniline, N-butyylaniline, N-methyl-2-methylaniline, N-methyl-2,6-dimethylaniline, N-methyl-2,4,6-trimethylaniline, and N-naphthylaniline. Preferable examples can include N-phenylethanolamine and N-ethylaniline.

[0020] In the present invention, the usage of secondary amine to be used here is not specifically limited, and is 0.01 to 5 percent by weight relative to the weight of the resulting polyphenylene ether. Preferably, the usage is 0.05 to 3 percent by weight. The phenolic compound to be used in the present invention is a compound having a structure represented by Formula (2),

[0021]

[Chemical formula 1]



[0022] (In Formula, R3 represents an alkyl group, a substituted alkyl group, an aralkyl group, a substituted aralkyl group, an aryl group, a substituted aryl group, an alkoxy group, or a substituted alkoxy group, R4 represents the same as that defined for R3 or, furthermore, a halogen, and R5 represents the same as that defined for R4 or, furthermore, hydrogen.) Examples thereof include 2,6-dimethylphenol, 2,3,6-trimethylphenol, 2-methyl-6-ethylphenol, 2,6-diethylphenol, 2-ethyl-6-n-propylphenol, 2-methyl-6-chlorophenol, 2-methyl-6-bromophenol, 2-methyl-6-isopropylphenol, 2-methyl-6-n-propylphenol, 2-ethyl-6-bromophenol, 2-methyl-6-n-butylphenol, 2,6-di-n-propylphenol, 2-ethyl-6-chlorophenol, 2-methyl-6-phenylphenol, 2,6-diphenylphenol, 2,6-bis-(4-fluorophenyl)phenol, 2-methyl-6-tolylphenol, and 2,6-ditolylphenol. These phenolic compounds may be used alone or in combination of at least two types. A small amount of phenol, o-cresol, m-cresol, p-cresol, 2,4-dimethylphenol, 2-ethylphenol, or the like may be contained substantially without any problem. Among these phenolic compounds, 2,6-dimethylphenol is particularly important.

[0023] In the method of the present invention, either the slurry polymerization method or the solution polymerization method can be selected as the oxidative polymerization method. In the slurry polymerization method, a single

solvent, in which the generated polyphenylene ether is not completely dissolved at a polymerization temperature, or a mixed solvent, in which the composition is adjusted by at least one type of good solvent for the polyphenylene ether and at least one type of poor solvent, is selected. In the solution polymerization, a single solvent or a mixed solvent, in which the generated polyphenylene ether is dissolved at a polymerization temperature, is selected. Example of solvents to be used will be described. Examples of usable good solvents for the polyphenylene ether include aromatic hydrocarbons, e.g., benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene; halogenated hydrocarbons, e.g., methylene chloride, chloroform, 1,2-dichloroethane, chlorobenzene, and dichlorobenzene; and nitro compounds, e.g., nitrobenzene. At least one type of them can be used alone or in combination. Examples of usable poor solvents for the polyphenylene ether include alcohols, e.g., methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, and tert-butanol; ketones, e.g., acetone and methyl ethyl ketone; ethers, e.g., diethyl ether; aliphatic hydrocarbons, e.g., hexane and cyclohexane; and, furthermore, water. At least one type of them can be used alone or in combination.

[0024] In the oxidative polymerization of the present invention, pure oxygen, a mixture of oxygen and an inert gas, e.g., nitrogen, in any proportion, air, or the like can be

used as oxygen to be supplied. Normal pressure is adequate for the pressure in the system during the reaction and, if necessary, either a reduced pressure or a pressure higher than normal pressure can be used. The present invention is characterized by using the slurry, in which a part of the polyphenylene ether resulting from the polymerization is deposited during the polymerization or after the polymerization, in the heat treatment. In the case where the polyphenylene ether produced by the slurry polymerization method is used, when the polyphenylene ether is completely dissolved at some temperature or more within the range of 50°C to 120°C, a temperature, at which the polyphenylene ether is not completely dissolved, must be selected as the heat treatment temperature, or a temperature within the range of 50°C to 120°C, at which the polyphenylene ether is present as a slurry, must be selected by further adding a poor solvent for the polyphenylene ether. In the solution polymerization, a poor solvent for the polyphenylene ether must be added in such a way that the polyphenylene ether is not completely dissolved at 50°C or low. For the heat treatment temperature, a temperature within the range of 50°C to 120°C, at which the polyphenylene ether is not completely dissolved, must be selected. However, a solvent composition, in which the polyphenylene ether is not dissolved at all within the temperature range

of 50°C to 120°C, cannot be used. If a solvent in which the polyphenylene ether is not dissolved at all is used, no reforming effect is exerted. If the polyphenylene ether is completely dissolved, although the polyphenylene ether having a low molecular weight is increased, the center position of the main peak of the molecular weight distribution of the polyphenylene ether produced in the polymerization and having a distribution in high molecular weights capable of maintaining the desired mechanical characteristics is significantly shifted to the low molecular weight side. Therefore, the controllability of operation is significantly deteriorated.

[0025] The temperature of heat treatment in consideration of the reforming effect is within the range of 50°C to 120°C. If the heat treatment is conducted at a temperature lower than 50°C, a substantial effect of reforming the polyphenylene ether is small and a significant improvement of the fluidity is not observed. If the temperature of heat treatment is higher than 120°C, the behavior of molecular weight reduction gets a high priority, and the behavior, which is the feature of the present invention, of a shift of the center position of the main peak of the molecular weight distribution of the polyphenylene ether to the high molecular weight side is not observed. A more preferable heat treatment temperature is within the range of 60°C to

90°C.

[0026] It is desirable that the amount of dissolution of the polyphenylene ether in the heat treatment is 0.01 to 40 percent by weight of the total weight of the polyphenylene ether. The type and the amount of solvent are not specifically limited as long as this condition is satisfied, except for solvents having high reactivity with the polyphenylene ether and, thereby, obstructing significantly the method of the present invention. Furthermore, it is desirable that the concentration of the polyphenylene ether relative to the total amount of the slurry is within the range of about 5 to 50 percent by weight in consideration of the operability, economy, and the like.

[0027] With respect to the heat treatment method, the atmosphere of the gas phase portion may be oxygen or air as long as the oxygen supplied during the polymerization is stopped. However, it is preferable that the heat treatment is conducted in an atmosphere substituted with an inert gas from the viewpoint of safety. The catalyst used for the polymerization or a reagent and the like used for the purpose of removing the catalyst may be contained as long as the supply of oxygen is stopped. Preferably, the heat treatment is conducted in the coexistence of a compound, e.g., ethylenediamine tetraacetic acid, for the purpose of deactivating the copper compound serving as the catalyst.

With respect to the pressure, the heat treatment can be conducted at normal pressure when the heat treatment is conducted at the boiling point of the solvent or lower. However, when the heat treatment is conducted at the boiling point or higher, a reflux device is connected, or the heat treatment can be conducted under pressure to maintain the heat treatment temperature. Preferably, the heat treatment is conducted through agitation to facilitate the mixing of the slurry.

[0028] The heat treatment time depends on a heat treatment temperature as well and, therefore, cannot be specified clearly. However, it is essential that the treatment is conducted for the time adequate for exerting the desired effect of reforming the polyphenylene ether. In general, about 10 minutes to 5 hours is an adequate degree, and excessively long time does not make sense. The mechanisms of the reaction for reducing the molecular weight and the reaction for increasing the molecular weight, which occur in the heat treatment, will be estimated. It is believed that a quinone compound generated as a byproduct in the oxidative polymerization of a phenolic compound involves in the reaction for reducing the molecular weight, as shown in Japanese Examined Patent Application Publication No. 61-20576. Furthermore, it is estimated that the quinone compound and the secondary amine represented by Formula (1)

of the present invention involve in the reaction for increasing the molecular weight observed specifically in the present invention, a specific reaction is effected on the deposited polyphenylene ether and, thereby, the above-described specific molecular weight distribution is manifested.

[0029] After the heat treatment is completed, the desired polyphenylene ether can be recovered from the mixture by using a known method. The thus produced polyphenylene ether is usefully applied to various thermoplastic resin compositions and the like. For example, it is applied to a composition with a polystyrene based resin or a polyamide resin. The compositions including the polyphenylene ether produced by the present invention can contain other additives, for example, plasticizers, stabilizers, ultraviolet absorbers, flame retardants, coloring agents, mold release agents, fibrous reinforcements, e.g., glass fibers and carbon fibers, and furthermore, fillers, e.g., glass beads, calcium carbide, and talc. For the stabilizers, phosphorous acid esters, hindered phenols, sulfur-containing antioxidants, alkanolamines, acid amides, dithiocarbamic acid metal salts, inorganic sulfides, metal oxides, and the like can be used alone or in combination. Any method is adopted as the method for mixing all constituents. For example, an extruder, a heating roll, a Banbury mixer, or a

kneader can be used.

[0030]

[Embodiments] The application of the present invention to industrially very important poly(2,6-dimethyl-1,4-phenylene)ether and properties of a polyphenylene ether/polystyrene based resin composition including the polyphenylene ether produced according to the present invention will be further specifically described below. However, the present invention is not limited to these examples.

[0031] The measurements were conducted under the following conditions.

① Solution viscosity of polyphenylene ether

The viscosity of the polyphenylene ether is determined by measuring a 0.5-g/dl chloroform solution under a condition of 30°C by using the Ubbelohde viscometer, and is indicated by η_{sp}/c .

② Molecular weight and molecular weight distribution of polyphenylene ether

A calibration curve is prepared with Gel Permeation Chromatography HL-802RTS produced by Toyo Soda Manufacturing Co., Ltd., through the use of standard polystyrenes, and the measurement is conducted. The polystyrenes having molecular weights of 264, 364, 466, 568, 2,800, 16,700, 186,000, and 1,260,000 are used. Columns, TSKgelG2500H_{XL}, TSKgelG3000H_{XL},

TSKgelG4000H_{XL}, and TSKgelG5000H_{XL}, each produced by Toyo Soda Manufacturing Co., Ltd., are connected in series, and are used. The measurement is conducted where the solvent is chloroform, the flow rate of the solvent is 0.9 ml/min, and the column temperature is 40°C. The measurement is conducted where the wavelength of UV of a detection portion is 254 nm for the standard polystyrene and 283 nm for the polyphenylene ether.

[0032] In both Example and Comparative example, resin compositions having the following compositions were formed from the produced polyphenylene ethers by the following manufacturing method, and the fluidity and the chemical resistance were compared. Blending of 43.1 parts by weight of polyphenylene ether, 12.9 parts by weight of homopolystyrene resin (Styron 685 produced by Asahi Kasei Corporation), 44.2 parts by weight of impact-resistant polystyrene resin (Styron 494 produced by Asahi Kasei Corporation), and stabilizers, 0.14 parts by weight of ZnO, 0.14 parts by weight of ZnS, and 0.14 parts by weight of tris(2,4-di-*t*-butylphenyl)phosphite was conducted, followed by mixing with a mixer. Thereafter, melt-kneading and extrusion were conducted with a 30-mm twin-screw extruder (PCM-30 produced by Ikegai Machinery Co.), and a strand was cut with a pelletizer, so that a resin composition in the shape of pellets was produced. The melt flow rate (MFR) was

measured with a melt flow indexer by using the resulting pellets. Furthermore, SSP was measured in the formation of a dumbbell molded piece with an injection molding machine (IS-80C produced by TOSHIBA MACHINE CO., LTD.) from the resin composition pellets. A dumbbell molded article was formed, and the chemical resistance was measured. The condition of each measurement item is as described below.

a. Measurement of fluidity

① MFR: The measurement was conducted at 250°C under a load of 10 kg based on ASTM/D1238. (Unit: g/10 min)

② SSP: A minimum gauge pressure required for molding an ASTM/D638 test piece was measured. Molding temperature 290°C. Mold temperature 80°C (Unit: kg/cm²)

b. Measurement of chemical resistance

A test piece of 4 mm in width, 2.4 mm in thickness, and 20 mm in length was formed. This test piece was mounted horizontally on a rack in such a way that a half of the test piece from the center was overhung. A load of 560 g in weight was applied to the overhang side, shaft grease was applied to the central portion of the test piece, and the time elapsed since the load was applied until the test piece was broken was measured.

[0033]

[Example 1] In a 5-l glass reactor, 0.10 g of cupric chloride dihydrate, 0.43 g of 35-percent hydrochloric acid,

8.0 g of N,N,N',N'-tetramethyl-1,3-diaminopropane, 3.0 g of N-ethylaniline, and 700 g of methanol were introduced. Furthermore, 300 g of 2,6-dimethylphenol and 540 g of butanol dissolved in 1,450 g of xylene were introduced. The reaction was conducted at 40°C for 3.5 hours while oxygen was supplied. The reaction mixture liquid was in a slurry state in which a part of polymers were deposited.

[0034] The copper complex in the active catalyst system was deactivated by adding 5.2 g of 10-percent by weight aqueous solution of ethylenediamine tetraacetic acid·tripotassium salt to the resulting reaction mixture liquid. A reflux tube was attached to the reactor, and heating and reflux were conducted at 70°C for 60 minutes while agitation was conducted. Small amounts of samples were taken from the reaction mixture liquid before and after the heating, methanol was added by a volume of 5 times that of the sample, followed by filtering and washing 3 times with methanol. The resulting product was vacuum-dried at 140°C for 1 hour, so that a polyphenylene ether powder was produced. The η_{sp}/c of the polyphenylene ether produced from the reaction mixture liquid before the heating was 0.54, and the η_{sp}/c of the polyphenylene ether produced from the reaction mixture liquid after the heating was 0.60. The molecular weight distributions of the polyphenylene ether before and after the heating are shown in Fig. 1.

[0035] The reaction mixture liquid after the heating was washed with methanol, and centrifugal separation was conducted. The polyphenylene ether containing the solvent was vacuum-dried at 140°C for 1 hour. A resin composition was prepared by using the polyphenylene ether after being dried, and the fluidity and the chemical resistance were evaluated. The results thereof are shown in Table 1.

[0036]

[Example 2] In a 500-ml glass reactor, 0.021 g of cupric chloride dihydrate, 0.090 g of 35-percent hydrochloric acid, 0.80 g of N,N,N',N'-tetramethyl-1,3-diaminopropane, 0.30 g of n-dibutylamine, 0.015 g of N-ethylaniline, and 70 g of methanol were introduced. Furthermore, 30 g of 2,6-dimethylphenol and 54 g of butanol dissolved in 145 g of xylene were introduced. The reaction was conducted at 40°C for 3.5 hours while oxygen was supplied. The reaction mixture liquid was in a slurry state in which a part of polymers were deposited.

[0037] The copper complex in the active catalyst system was deactivated by adding 1.1 g of 10-percent by weight aqueous solution of ethylenediamine tetraacetic acid·tripotassium salt to the resulting reaction mixture liquid. A reflux tube was attached to the reactor, and heating and reflux were conducted at 70°C for 60 minutes while agitation was conducted. Small amounts of samples were taken from the

reaction mixture liquid before and after the heating, methanol was added by a volume of 5 times that of the sample, followed by filtering and washing 3 times with methanol. The resulting product was vacuum-dried at 140°C for 1 hour, so that a polyphenylene ether powder was produced. The η_{sp}/c of the polyphenylene ether produced from the reaction mixture liquid before the heating was 0.39, and the η_{sp}/c of the polyphenylene ether produced from the reaction mixture liquid after the heating was 0.41. The molecular weight distributions of the polyphenylene ether before and after the heating are shown in Fig. 2.

[0038]

[Comparative example 1] In a 5-l glass reactor, 0.21 g of cupric chloride dihydrate, 0.90 g of 35-percent hydrochloric acid, 8.0 g of N,N,N',N'-tetramethyl-1,3-diaminopropane, 3.0 g of n-dibutylamine, and 700 g of methanol were introduced. Furthermore, 300 g of 2,6-dimethylphenol and 540 g of butanol dissolved in 1,450 g of xylene were introduced. The reaction was conducted at 40°C for 3.5 hours while oxygen was supplied. The reaction mixture liquid was in a slurry state in which a part of polymers were deposited.

[0039] The copper complex in the active catalyst system was deactivated by adding 11 g of 10-percent by weight aqueous solution of ethylenediamine tetraacetic acid·tripotassium salt to the resulting reaction mixture liquid. A reflux

tube was attached to the reactor, and heating and reflux were conducted at 70°C for 60 minutes while agitation was conducted. Small amounts of samples were taken from the reaction mixture liquid before and after the heating, methanol was added by a volume of 5 times that of the sample, followed by filtering and washing 3 times with methanol. The resulting product was vacuum-dried at 140°C for 1 hour, so that a polyphenylene ether powder was produced. The η_{sp}/c of the polyphenylene ether produced from the reaction mixture liquid before the heating was 0.49, and the η_{sp}/c of the polyphenylene ether produced from the reaction mixture liquid after the heating was 0.46. The molecular weight distributions of the polyphenylene ether before and after the heating are shown in Fig. 3.

[0040] The reaction mixture liquid after the heating was washed with methanol, and centrifugal separation was conducted. The polyphenylene ether containing the solvent was vacuum-dried at 140°C for 1 hour. A resin composition was prepared by using the polyphenylene ether after being dried, and the fluidity and the chemical resistance were evaluated. The results thereof are shown in Table 1.

[0041]

[Comparative example 2] Polymerization was conducted as in Example 1. The copper complex in the active catalyst system was deactivated by adding 5.2 g of 10-percent by weight

aqueous solution of ethylenediamine tetraacetic acid·tripotassium salt to the reaction mixture liquid. The resulting reaction mixture liquid was washed with methanol without conducting any heat treatment and the like, and centrifugal separation was conducted. The polyphenylene ether containing the solvent was vacuum-dried at 140°C for 1 hour. The η_{sp}/c of the resulting polyphenylene ether was 0.54. A resin composition was prepared by using the polyphenylene ether after being dried, and the fluidity and the chemical resistance were evaluated. The results thereof are shown in Table 1.

[0042]

[Comparative example 3] In a 500-ml glass reactor, 0.021 g of cupric chloride dihydrate, 0.090 g of 35-percent hydrochloric acid, 0.80 g of N,N,N',N'-tetramethyl-1,3-diaminopropane, 0.30 g of N-ethylaniline, 0.060 g of trioctylammonium chloride, and 13 g of methanol were introduced. Furthermore, 30 g of 2,6-dimethylphenol dissolved in 242 g of toluene was introduced. The reaction was conducted at 40°C for 3.5 hours while oxygen was supplied. The reaction mixture liquid was in a homogeneous solution state.

[0043] The copper complex in the active catalyst system was deactivated by adding 1.1 g of 10-percent by weight aqueous solution of ethylenediamine tetraacetic acid·tripotassium

salt to the resulting reaction mixture liquid. A reflux tube was attached to the reactor, and heating and reflux were conducted at 50°C for 60 minutes while agitation was conducted so as to deposit polymers. Small amounts of samples were taken from the reaction mixture liquid before and after the heating, methanol was added by a volume of 5 times that of the sample, followed by filtering and washing 3 times with methanol. The resulting product was vacuum-dried at 140°C for 1 hour, so that a polyphenylene ether powder was produced. The η_{sp}/c of the polyphenylene ether produced from the reaction mixture liquid before the heating was 0.87, and the η_{sp}/c of the polyphenylene ether produced from the reaction mixture liquid after the heating was 0.58. The molecular weight distributions of the polyphenylene ether before and after the heating are shown in Fig. 4.

[0044]

[Advantages] According to the method of the present invention, by heat-treating the polymerization liquid, the center position of the main peak of the molecular weight distribution of the polyphenylene ether produced in the polymerization can be shifted to the high molecular weight side and, simultaneously, the low molecular weight portion can be increased. Therefore, excellent mechanical characteristics of the polyphenylene ether can be improved and, simultaneously, the fluidity can be improved.

Furthermore, according to this method, the total molecular weight is hardly changed before and after the heating since the increase in molecular weight and the reduction in molecular weight are coincident. Consequently, since there is no need to increase the concentration of the active catalyst system in the reaction system, the amount of catalyst to be used is reduced and the productivity improvement is facilitated as well.

[0045]

[Table 1]

		Example 1	Example 2	Comparative example 1	Comparative example 2	Comparative example 3
Constituent features	R1R2NH	N-ethylaniline	N-ethylaniline + dibutylamine	dibutylamine	N-ethylaniline	N-ethylaniline
	Form of polyphenylene ether	deposition	deposition	deposition	deposition	homogeneous solution
	Heating with no supply of oxygen (50°C to 120°C)	no supply of oxygen (70°C)	no supply of oxygen (70°C)	no supply of oxygen (70°C)	no heat treatment	no supply of oxygen (50°C)
Molecular weight distribution	High molecular weight peak	shift to high molecular weight side	shift to high molecular weight side	no change	-	entire shift to low molecular weight side
	Low molecular weight peak	newly generated	newly generated	newly generated	-	
		0.54	0.39	0.49	0.54	0.87
Properties of resin composition	η_{sp}/c (dl/g)	Before heating				
		After heating	0.41	0.46	-	0.58
	Fluidity (g/10min)	MFR	-	6.8	7.1	-
		SSP (kg/cm)	-	44	40	-
Result of discussion	Chemical resistance	6.8	-	2.8	0.4	-
	Breaking time (hr)					
Result of discussion		satisfy needs	satisfy needs	aromatic secondary amine is necessary	heating is necessary	homogeneous solution does not satisfy needs

[Brief Description of the Drawings]

[Fig. 1] Molecular weight distribution of the polyphenylene ether in Example 1: A solid line represents the distribution before the heat treatment and a broken line represents the distribution after the heat treatment. The horizontal axis indicates the logarithmic value of the molecular weight, and the vertical axis indicates the value 5.5 times larger than the differential molecular weight distribution value. (The same holds true for Figs. 2 to 4.)

[Fig. 2] Molecular weight distribution of the polyphenylene ether in Example 2: A solid line represents the distribution before the heat treatment and a broken line represents the distribution after the heat treatment.

[Fig. 3] Molecular weight distribution of the polyphenylene ether in Comparative example 1: A solid line represents the distribution before the heat treatment and a broken line represents the distribution after the heat treatment.

[Fig. 4] Molecular weight distribution of the polyphenylene ether in Comparative example 3: A solid line represents the distribution before the heat treatment and a broken line represents the distribution after the heat treatment.